

Atomic-scale study of hydrodesulfurization model catalysts

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Introduction

The production of clean transport fuels by hydrotreating and especially hydrodesulfurization (HDS) has recently attracted increased attention due to the introduction of new environmental legislation regarding fuel specifications and technological requirements of high-purity fuels. In order to meet the new stringent demands there is a need to understand and improve HDS catalysts. It is generally accepted, that the HDS activity is related to the presence of so-called Co-Mo-S structures which consist of small MoS₂ nanoclusters with promoter atoms located near the edges¹. Controversy prevails, however, since the traditional spectroscopy-based techniques for catalyst characterization provide no conclusive information regarding the cluster morphology, catalytically relevant edge structures, active sites or the promotional effect of Co.

To aid the understanding of the industrial catalyst, new insight has been gained from studies of catalyst model systems by applying surface science techniques. In a series of studies, we have successfully used high-resolution Scanning Tunneling Microscopy (STM) to study the real space atomic structure of single-layer MoS₂ nanoclusters synthesized on an inert Au(111) substrate as a model system for the HDS catalysts. The insight gained from the STM studies gives a hitherto unprecedented view of the atomic details of the MoS₂ nanoclusters¹.

Experimental

The experiments are performed in an ultra-high vacuum chamber equipped with the unique home-built high-resolution Aarhus STM, which has demonstrated the capability of providing atom-resolved images of a large variety of systems on a routine basis². The Au(111) surface is chosen as a model substrate for two reasons. Gold is chemically rather inert, and furthermore gold belongs to the class of metal the surface of which reconstructs in its clean state. Specifically the Au(111) has a characteristic "herringbone" reconstruction pattern, which is ideal for providing nucleation sites for the deposited metal atoms and thereby dispersing submonolayer amounts of material into Mo or Co nanoclusters^{3,6}. An ensemble of ~30 Å wide crystalline MoS₂ nanoclusters were formed

by initially depositing Mo (10% coverage) in an background H₂S (10⁻⁶ mbar) followed by high-temperature annealing (673K) for 15 min while maintaining the sulfiding atmosphere.

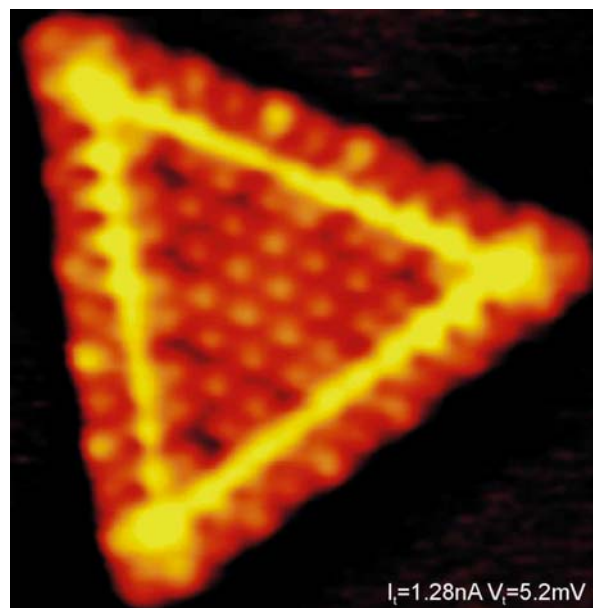


Figure 1: Atom-resolved ($41 \times 42 \text{ Å}^2$) STM image of an unpromoted single-layer MoS₂ nanocluster synthesized on a Au(111) template³.

Results and Discussion

High resolution STM images reveal new insight into the atomic details of the MoS₂ nanostructures (**Figure 1**). Contrary to our expectations based on the structure of bulk MoS₂, the majority of the nanoclusters are found to exhibit a pronounced triangular morphology. The shape of a single-layer MoS₂ cluster is in principle governed by the relative stability of two low-index types of edge terminations, an S-edge and a Mo-edge. Equal stability between these would produce a perfectly hexagonal cluster. The observed triangular morphology implies, however, that one type of edge termination is considerably more stable than the other.

It is important to point out that STM to a first approximation measures contours of constant local density of states (LDOS) in the surface projected onto the apex of the STM tip, and that STM images therefore reflect a rather complicated convolution of both geometric and electronic structure. This is especially true for adsorbates on surfaces, oxide or sulfide materials and in the STM images of the MoS₂ nanoclusters we indeed observe two examples of this. First of all, we observed the protrusions at the edge of the MoS₂ triangle to be out of registry with the basal plane S atoms. Second, a pronounced bright brim extending all the way around the perimeter of the triangular MoS₂ nanoclusters is identified in the STM image. Rather than geometrical effects pertaining to the triangular MoS₂ cluster (**Figure 1**), these features reflect subtle electronic changes at the edges, and are therefore attributed to distinct electronic features existing only near the edges, i.e. one-dimensional electronic edge states. The brim is seen in the STM image to be highly localized in the direction perpendicular to the edge and furthermore exhibits a very high electronic conductivity. It can thus be associated with a one-dimensional nanosized, metallic wire².

In density functional theory (DFT) calculations of the band structure of the MoS₂ edges we indeed find the existence of several

localized electronic edge states pertaining to the Mo edge. By comparing the detailed atomic-scale structure observed in the experimental images with STM simulations resulting from the DFT calculations (**Figure 2**) we have confirmed that electronic edge states are responsible for the features observed at the edges of the MoS₂ triangles and we have identified the edge termination as the Mo edge fully saturated with S dimers^{3,4}.

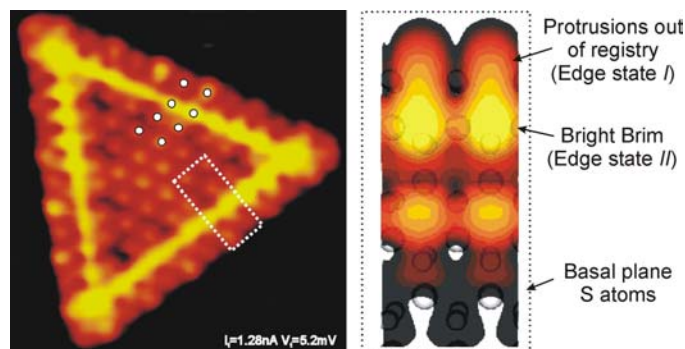


Figure 2: Left: Experimental STM image. White dots denote the position of protrusions on the MoS₂ nanocluster. Right: STM simulation (Tersoff-Hamann) of part of the Mo edge fully saturated with S dimers.

By means of the STM we have recently investigated the interaction of the MoS₂ clusters with thiophene (C₄H₄S) - a typical sulfur containing molecule widely used to test HDS reactivity. Upon adsorption of thiophene molecules we find in STM images that relatively inert molecules like thiophene preferentially interact with unusual sites located near the edges. Interestingly, we find that this interaction is modified by the presence of hydrogen species, and that the adsorption serves as an initial activation of thiophene molecules during catalytic hydrotreating reactions. This is followed by extrusion of sulfur at, for instance, edge vacancies, provided by reaction with gaseous hydrogen. We have exploited the capability of the STM to image in real-space these active sites on the atomic-scale with STM and investigated the energetics of the reaction with DFT calculations. The results thus provide new detailed insight into the reaction mechanism resulting in the extrusion of sulfur in the HDS process⁵.

The industrial MoS₂-based HDS catalysts are typically promoted with Co which enhances the catalytic activity by more than an order of magnitude. By applying an approach similar to the unpromoted MoS₂ experiments described above we have also obtained the first atomic-scale images of the structure of Co-Mo-S nanocrystals⁶. The idea behind our synthesis of Co-Mo-S is first to form MoS₂ embryos on the Au(111) surface followed by capping of these nanoclusters to facilitate the addition of Co to the edges of MoS₂ nanocrystals.

High resolution STM images of the resulting CoMoS structures reveal that the presence of the Co atoms has a dramatic influence on the morphology of the single-layer MoS₂ clusters (**Figure 3**). This surprising morphological transition, from triangular to hexagonally truncated, appears to be driven by a preference for Co to be located at only one type of MoS₂ edges - the S edge. The STM results also provide direct information on changes in the local electronic environment neighboring the Co edge atoms. This novel insight into the atomic and electronic structure may be important for understanding the promoting role of Co.

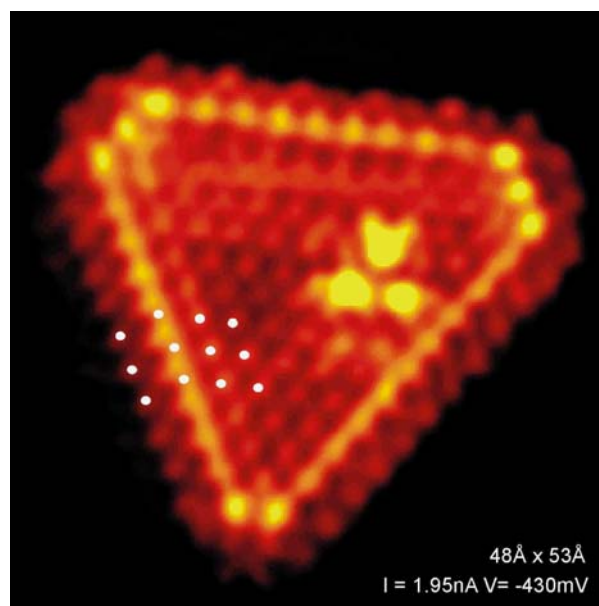


Figure 3: Atom-resolved STM image (48x53Å²) of a promoted Co-Mo-S nanocluster⁶ supported on Au(111).

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